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# Structural properties of low density liquid selenium

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**Abstract** We present extensive results of Reverse Monte Carlo (RMC) simulation of the static structural properties of liquid selenium from 573K to 1773K based on the diffraction data of Inui *et al* (*J. Non Cryst Solids* **250-252**, 519 (1999)) In all cases, the positions of 5000 atoms in a configuration box were altered until the resulting static structure factor $S(q)$ was in agreement with the experimental one From the simulations, we were able to extract information on the temperature dependence of the pair distribution function $g(r)$, bond angle correlation $b(\cos\theta)$ and coordination number distribution P(N). From our calculations, we deduce that with increase in temperature, there is a decrease in the fraction of two-fold coordinated atoms indicative of a destruction of the chain like structure of Se Furthermore, our results indicate that the transition from a semiconducting to a metallic state with increasing temperature is accompanied by structural changes

**Keywords** Liquid selenium, structural properties, reverse Monte Carlo simulation

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## 1. Introduction

At room temperature and pressure, selenium is a semiconductor. At higher temperatures, the decrease of density brings about a semiconductor to metal (SC-M) transition [1] instead of a metal to non-metal one. This result is quite interesting in the sense that it is in contradiction to established understanding. Experimental results [1,2] indicate that the semiconductor to metal transition occurs at a temperature $\approx$ 1500K and atomic density = 0.025 Å$^{-3}$ which is a temperature significantly lower than that at the critical point ($T_c$ = 1892 K, $P_c$ = 383 bar $\rho_c$ = 0.0141 Å$^{-3}$) [3]. A great deal of experiment using X-ray diffraction, X-ray absorption fine structure (XAFS) and the extended X- ray absorption fine structure (EXAFS) [1-3] has been performed on expanded Se. In addition, theoretical efforts using *ab-initio* computer simulation [4-9] and tight binding models [10-12] have been utilized to explain the nature of the SC-M transition.

With regards to the physical structure of crystalline Se, it is well known that this arises as a result of the Peierls distortion of a simple cubic structure [13]. It has a trigonal structure consisting of hexagonal arrays of helical chains of atoms that are 2-fold coordinated. It is classified as a semiconductor because the distortion opens up a gap in the density of states (DOS) at the Fermi level. With increase in pressure, the Peierls distortion reduces the gap in its DOS as a result of an increase in the number of first nearest neighbours. In addition, it is well known that the SC-M transition is characterized by a decrease in the electrical resistivity with volume expansion and moreover, that the metallic state appears when the average chain length becomes very short. A useful inference that can be drawn from this is that the transition can be correlated with a distortion of the chain structure [14].

Despite the wealth of information that has been obtained from the various kinds of *ab-initio* and other studies, it is still obvious that the microscopic mechanism for the observed SC-M transition is not yet fully understood. Arising from this, one is of the view that a study covering all temperatures and pressures at which structural information exists, could yield some useful insight into the nature of the SC-M transition. This follows from the fact that the Reverse Monte Carlo (RMC) model

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would be expected to give a detailed insight to the atomic structure that would be compatible with the available diffraction data. This is rather hard within the framework of molecular dynamics because of the difficulty of obtaining reliable interatomic potentials spanning such varying ranges of temperature and pressure.

We therefore, propose in the current paper to model the static structure factor $S(q)$ of Se using the RMC model. For the present calculations, all we need as input data are the experimental structure factors obtained from diffraction data and from that we can build up a 3-dimensional model of the structure that agrees quantitatively with the diffraction data. Since the model is fitted to the data, there must be good agreement, unless the data contains significant systematic errors.

Inui *et al* [1] have recently performed X- ray diffraction measurements on the structure factor of Se at 9 temperatures and pressures from 573 to 1773K using synchrotron radiation. Just as has been done for other expanded systems such as Hg and Cs [15, 16], we propose in the current paper, to use the RMC model to obtain more information about the structural properties of Se than can be obtained from pure structural measurements.

Thus, from our current simulations, we intend to obtain information such as the coordination number ($N_t$), distribution, the bond angle distribution and also the ring distribution. All these are expected to compliment the information obtained from the experimental structural investigation.

We note that some work have already been done trying to develop structural models for Se using the RMC model [17,18] at two temperatures and we intend to compare our more detailed results with them. The structure of the current paper is as follows: in the next section, we give a brief description of the RMC model, followed by a presentation of our results and its analysis for selenium. We conclude the paper with a summary of our important deductions.

## 2. RMC modelling

Reverse Monte Carlo (RMC) modelling is a technique that was developed [20, 21] to allow detailed information on liquid and amorphous materials to be obtained from diffraction data. Basically, this is done by minimizing the difference between experimental and calculated structure factors rather than energy as is the case in Metropolis Monte Carlo analysis. One important advantage of this is that one does not need interatomic potentials. Considering the difficulty of obtaining them especially for the present case of varying temperature, pressure and density, it is quite obvious that it is a very important advantage. With the technique of RMC, the positions of atoms in a configuration obeying specific boundary conditions are varied until the agreement with the experimental data does not improve further. The RMC algorithm could be described by the four steps :

(i) Define a cubic box with an initial configuration which is a three - dimensional array of N atoms in a cube of side L, such that the experimental number density is given by $N/L^3$. The initial configuration in addition represents atomic positions with periodic boundary conditions. Ideally, one is expected to use the microscopic atomic density which is,however, often not available and has to be estimated. Compare the calculated structure factor from this configuration with the experimental value using

$$\chi^3 = \sum_t \left[S_{mod}(q_t) - S_{expt}(q_t)\right]^2 / \sigma^2, \qquad (1)$$

where $S_{expt}(q_t)$ is the experimentally measured structure factor, $S_{mod}(q_t)$ the model one and $\sigma$ is a measure of the experimental error.

(ii) Move an atom at random and compute a new value of $S_{mod}(q_t)$ and thus a new $\chi^2$, let us call this $\chi'^2$

(iii) if $\chi'^2 < \chi^2$ , move is accepted. On the other hand $\chi'^2 > \chi^2$, the move is accepted with probability $\exp\left(-\left(\chi'^2 - \chi^2\right)/2\right)$, otherwise it is rejected

(iv) Repeat from step (ii).

These steps are repeated until $\chi^2$ is sufficiently small and oscillates around an equilibrium value. At this point the configuration for which $S_{mod}(q_t)$ agrees with $S_{expt}(q_t)$ within the limits of experimental error, can be evaluated.

In the present calculations, to simulate the structure of Se we start with an initial configuration of 5000 atoms arranged randomly but allowed to move at a minimum distance apart corresponding to the closest approach of two atomic centres. The modelling was done using the structure factors obtained from X - ray diffraction studies of Inui *et al* [1]. Table 1 shows the relevant temperatures and densities used in the present

**Table 1.** Table of densities used in the current simluations [1]

| T(K) | $p$ (g/cm$^3$) | $p$(Å$^{-3}$) | $P$ (bar) |
|---|---|---|---|
| 573 | 3.90 | 02974 | 10 |
| 873 | 3.69 | .02814 | 796 |
| 1073 | 3.52 | .02684 | 802 |
| 1273 | 3.36 | .02562 | 818 |
| 1373 | 3.29 | .02509 | 823 |
| 1473 | 3.25 | .02478 | 828 |
| 1573 | 3.21 | .02448 | 833 |
| 1673 | 3.16 | .02410 | 838 |
| 1773 | 3.11 | .02371 | 843 |

calculation and are taken from [1]. An initial RMC modelling of the data was done using the experimental data, however at temperatures of 1573K and higher, the shape of the resulting pair distribution function $g(r)$ was strange in the sense that it produced some unphysical spikes in the low $r$ region. This appears to be due to some small errors in the data, and probably arises as a result of a non-constant background possibly from the saphire cell used to deduce the structure factor of liquid Se. It is quite possible that this effect is more pronounced at high temperatures.

In order to reduce the effects of the possible errors, we have used a simple modification of the formal reverse Monte Carlo routine. Essentially, what we did was to determine $g(r)$ using the program MCGR [19] with the constraint that $g(r) = 0$ for $r < 2.0$ Å. The constraint makes it possible to refine possible errors from a non-constant background used in evaluating the experimental data. The difference is not that significant as is shown in Figure 1. We then used the RMC to fit the $S(q)$ derived by using MCGR, rather than those obtained from the original data. The difference between the two sets of data (experimental and MCGR derived) are quite small. The procedure we adopted here, however, enables us to remove the occurrence of the unphysical behaviour of $g(r)$ at higher temperatures and possibly most of the modulations. We are of the opinion that whatever errors are not removed by these scheme would not affect our conclusions in any significant way.

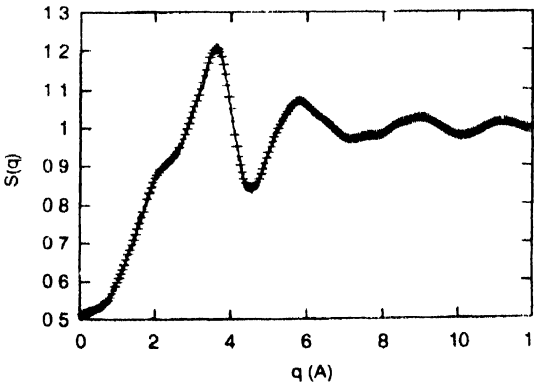


**Figure 1.** Structure factor for Se at 1373K, full curve (MCGR fit), symbols (experimental data [1]).

In the present simulations, we follow the philosophy in Ref. [18] which indicates that there is no experimental or theoretical evidence to suggest a very specific structure for selenium. Thus in all cases, we used a starting configuration in which the atoms are placed at random positions in the simulation box and then move them until the constraint on closest distance of approach was satisfied. In this way, we are able to generate a model which is not biased towards a structure with any specific features. In all cases, we used a very small value of $\sigma = 0.002$ in order to get a very good fit to the experimental data.

By a close analysis of the modelled $g(r)$, we discovered that a slightly larger distance of closest approach was essential up to about 873 K. This was in contrast to the higher temperatures where it appears as if the constituent atoms involved in the simulation, have enough energy to approach each other more closely. Thus arising from the above, in the simulations, the random atomic moves were limited by a cut-off distance of 2.1 Å at temperatures of 573 and 873K and 2.0 Å at higher temperatures.

In all cases, the RMC was run until there was convergence. In this context, the convergence is achieved when the value of $\chi^2$ remains virtually unchanged. In each case, we can determine from the final configuration, the static structure factor $S(q)$, pair distribution function $g(r)$, bond angle correlation $b(\cos\theta)$ and coordination number distribution $P(N)$. An analysis of these quantities makes it possible to obtain more information on the nature of expanded selenium than what is obtainable from experimental measurements of the static structure.

## 3. Results and analysis

We now try to present and analyze the results obtained from the RMC simulation of selenium at the temperatures given in Ref [1]. Figure 2 shows the fits to the X - ray diffraction data for $S(q)$ at all temperatures. From a perusal of the graphs, it is quite obvious that the RMC fits agree very well with the experimental values across the whole temperature scale. This is obvious from the fact that at almost all temperatures, it is impossible to distinguish between the solid line and the line with symbols in the $x$. In all cases, we end up with a situation in which the goodness-of-fit indicator for the structure factor was about 2%. From this, we can infer that our resulting RMC configurations can be used with confidence to discuss the nature of the short and medium range order in liquid selenium.

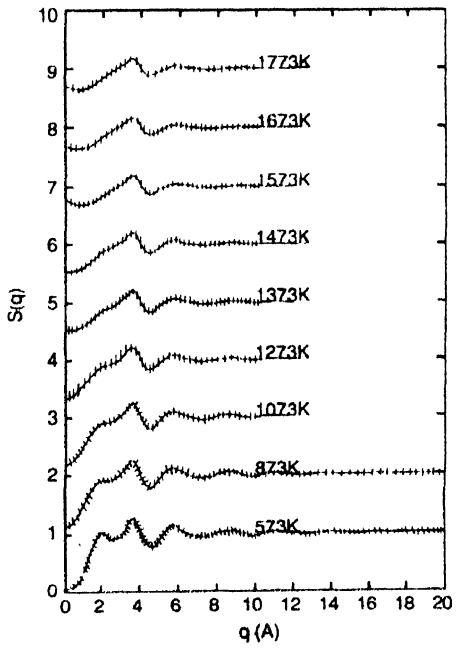


**Figure 2.** Temperature variation of $S(q)$ with $q$ (Å$^{-1}$) (symbols) - RMC, (full line) experimental values [1] The structure factors are for 573K (lowest) to 1773K (uppermost).

The pair distribution functions $g(r)$ as derived from RMC simulation are shown in Figure 3 and compared with the experimental values obtained by a Fourier transform of $S(q)$. As is to be expected, the position of the 1st peak in $g(r)$ ($\approx$ 2.3 Å) is to a large extent invariant with temperature, while that of the first minimum moves perceptably with temperature by almost 0.2 Å from the lowest to the highest temperature under consideration. The lack of a significant change in the peak position indicates that the nature of the bonding remains unchanged with increase in temperature. Regarding the structure of $g(r)$, the general effect of an increase in temperature in decreasing the height of the first peak and reducing the depth of the first minimum, is reproduced by our calculations.

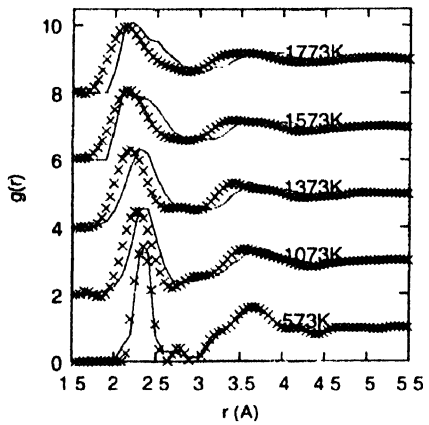


**Figure 3.** Temperature variation of $g(r)$ with $r$ (Å) Symbols are $g(r)$ obtained from Fourier transform of experimental $s(q)$ while solid lines are results obtained from RMC

Essentially, the latter implies a disruption in the chain structure of Se at higher temperatures. We take the view that the sharpness of the first peak of $g(r)$ in Se is due to the presence of the chain like structure. Interestingly enough, the RMC simulation indicates that the first peak of $g(r)$ is sharp even at the highest temperature, this is the evidence of the existence of a chain like structure even at those high temperatures. By interpolation, one would thus expect that the chain-like structure would persist in the metallic state.

A comparison of the $g(r)$, experimental and theoretical, shows that the fit gets worse in comparison with experiment at high temperatures. Nevertheless, the quality of the computed $g(r)$ is quite comparable to that obtained from tight binding calculations [12] which is currently one of the best techniques for treating semiconductors from a theoretical point of view. In addition, we note that the quality of the result for $g(r)$ at 573K is quite comparable to that obtained from previous simulations at such temperatures [18]. An inference that can be drawn from here is probably that the agreement between RMC generated and fourier transform $g(r)$ gets worse with increasing temperature. We observe that we could obtain a better fit for $g(r)$ by imposing the condition that the RMC reproduces both the $S(q)$ and the $g(r)$ as was done in [19]. However, we observe that this usually results in poorer agreement with experimental $S(q)$ which happens to be the only experimental data available to us

An additional point that can be made about the $g(r)$ is that at 573 K, the first minimum is almost zero and with increasing temperature, the value increases to a value quite close to those for metallic systems. The first minimum can be considered as a measure of how much the chain structure is disrupted. At the lowest temperature, it is expected to consist of $\approx 10^5$ atoms and with increasing temperature, this chain gets disrupted when the number of atoms is expected to be of the order of 10 [22]

In the current context, we define a chain as a series of 2-fold coordinated atoms terminated at both ends by under-or over-coordinated atoms.

In order to have some kind of visualization of the structural change in the SC-M transition, we try to investigate the variation in the coordination number with temperature. One notes that there are various ways of defining $N_c$ depending on the cut off distance which is used to define what constitutes a neighbour In the present calculation, for the determination of the nearest neighbour distance and the bond-angle distribution, we define the nearest neighbours of an atom as those at a distance less than a certain value from the reference atom. For this distance we have taken a value corresponding to the value of the position of the first minimum in $g(r)$.

The average coordination number $N_c$ at each temperature was then obtained from the calculated atomic configurations by integrating $4\pi\int_0^{r_1} r^2\rho g(r)$, where $\rho$ is the number density of the atoms and $r_1$ is the position of the first minimum in $g(r)$ The temperature variation is indicated in Table 2. It is quite obvious that the average coordination number remains close to two in the semiconducting region and increases gradually with temperature even in the region of the SC-M transition. Finally, one observes that it is a little greater than 2 in the metallic region. It is also observable that the coordination number is the highest at 1573K , a temperature close to the transition, though

**Table 2.** The temperature variation of the coordination number $N_c$ obtained from RMC simulation.

| T(K) | $N_c$ |
|---|---|
| 573 | 1.95 |
| 873 | 2.14 |
| 1073 | 2.12 |
| 1273 | 2.15 |
| 1373 | 2.23 |
| 1473 | 2.35 |
| 1573 | 2 49 |
| 1673 | 2.24 |
| 1773 | 2.40 |

we do not attach much significance to this. The temperature variation of $N_c$ is partially related to the change in the position of the first minimum in $g(r)$, this is found to increase from 2.80 Å in the semiconducting to 3.0 Å in the metallic state.

Next we deduce some information from the variation of the nearest neighbour number distribution with temperature Table 3. Several useful deductions can be made from this.

**Table 3.** Coordination number distribution for the temperatures of interest The first column refers to the coordination number shell The other numbers are in percentages.

| T(K) | 573 | 873 | 1073 | 1273 | 1373 | 1473 | 1573 | 1673 | 1773 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 6 14 | 5.52 | 6.24 | 6 62 | 7.06 | 5.90 | 5 74 | 7.56 | 6 52 |
| 1 | 25 66 | 23 42 | 23 90 | 24 08 | 23 58 | 21.06 | 18 54 | 23 50 | 20 20 |
| 2 | 40 84 | 35 58 | 34 88 | 32 90 | 30 34 | 29.36 | 28 48 | 29 10 | 28 96 |
| 3 | 22 18 | 24.96 | 23.90 | 23 76 | 23.08 | 25 74 | 24.94 | 23.00 | 24.08 |
| 4 | 4 82 | 8 72 | 9.22 | 9.76 | 11 44 | 12 48 | 15.18 | 11 98 | 13 38 |
| 5 | 0 36 | 2.60 | 1 68 | 2.48 | 3 26 | 4 56 | 5 26 | 3 80 | 5 42 |
| 6 | 0 00 | 0 28 | 0 18 | 0.36 | 1 02 | 0.72 | 1 48 | 0 88 | 1 06 |
| 7 | 0 00 | 0 02 | 0 00 | 0 04 | 0 20 | 0.16 | 0 34 | 0 18 | 0 32 |
| 8 | 0 00 | 0.00 | 0 00 | 0.00 | 0 02 | 0.02 | 0.04 | 0 00 | 0 04 |

Firstly, one observes with regards to specific aspects of the calculations, that at all temperatures, the majority of the atoms are 2-fold coordinated. As the temperature increases, there is an increased tendency for the atoms to be under ($N_c < 1$) or over ($N_c > 2$) coordinated, with some of the atoms being 8-fold coordinated at the highest temperature. This is in contrast with the situation at the initial temperature where most of the atoms are a maximum of 5-fold coordinated. The observed, gradual reduction in the fraction of 2-fold coordinated atoms with increasing temperature looks indicative of a destruction in the chain-like structure that is expected to be predominant at low temperatures.

It is fairly obvious that there is an increased tendency for atoms to move away from the state with a coordination number of 2 as the temperature increases. We however, observed that even with this drift, the average coordination number is still less than 3, unlike the situation in Te in which the coordination number changes from 2 to 3 as temperature increases [1].

The results obtained by doing a chain statistics of the RMC obtained configurations is reported in Table 4. As previously stated, one expects that close to the melting point, the chains should involve about $10^5$ atoms, however, in accord with recent molecular dynamics and tight binding calculations [10, 23] which suggest that the chains are short, we found between 2.9 and 2.5 bonds per chain in our current RMC model of Se.

Based on the fact that the calculations indicate a preference for 2-fold coordination, we also performed an analysis of the ring- like structure of selenium. For the purpose of the current calculations, we shall consider as a ring, any shortest closed path of bonds connecting a Se atom with its neigbours. Because of the large number of atoms used in our calculations and thus the large size of the simulation box, we are able to check the existence of rings constituted of upto 12 Se atoms. We note that the rings evolve naturally in the present calculations and are not promoted by the program in any way

**Table 4.** Chain statistics for Se. The first column refers to the number of bonds per chain and all other numbers are in percentages

| T(K) | 573 | 873 | 1073 | 1273 | 1373 | 1473 | 1573 | 1673 | 1773 |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 51 16 | 58 33 | 54.91 | 59 22 | 57 23 | 62.05 | 59 13 | 65 45 | 62 84 |
| 3 | 25 58 | 21 43 | 26 59 | 25 70 | 27 17 | 22 89 | 27 83 | 22 51 | 20 95 |
| 4 | 13 02 | 12.50 | 10.98 | 9 50 | 11.56 | 10 24 | 6 96 | 8 38 | 8 11 |
| 5 | 5 58 | 5 95 | 6 36 | 3 35 | 2 89 | 3 61 | 5 22 | 1 57 | 5 41 |
| 6 | 1 86 | 1 19 | 1 16 | 0 56 | 1 16 | 0.60 | 0 87 | 2 09 | 1 35 |
| 7 | 0 47 | 0 60 | 0 00 | 0 56 | 0 00 | 0 60 | 0 00 | 0 00 | 1 35 |
| 8 | 0 93 | 0 00 | 0 00 | 1 12 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 |
| 9 | 0 93 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 |
| 10 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 |
| 11 | 0 47 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 | 0 00 |

An analysis of the ring structure is presented as a table in order to make it easier to visualize the results, they are as presented in Table 5. A perusal of the table indicates that apart from the trivial triangular 3 member ring arrangement, the 4 , 5 and greater than 12 membered rings mostly occur in Se. It is also observable that with an increase in temperature, the percentage of rings constituted of more than 12 Se atoms reduces significantly down to about half the value at the melting point. This is the indication of an increase in the metallic behaviour of Se as the temperature increases. The geometry of the configurations obtained does not , however, correspond to the $Se_8$ rings which are the building blocks of liquid and solid monoclinic Se.

**Table 5.** Ring statistics for Se in the present RMC simulation The first column refers to the number of bonds per ring while the other numbers are in percentages

| T(K) | 573 | 873 | 1073 | 1273 | 1373 | 1473 | 1573 | 1673 | 1773 |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 20 03 | 26 06 | 26 46 | 27 93 | 28.93 | 30 05 | 31 77 | 30 25 | 31 09 |
| 4 | 3 43 | 7 44 | 7 13 | 8 62 | 11 35 | 11 34 | 13 15 | 11 71 | 13 11 |
| 5 | 1 22 | 3 31 | 2 66 | 3 72 | 5 45 | 5 37 | 6 21 | 5 45 | 6 98 |
| 6 | 1.02 | 1.69 | 1 70 | 2.37 | 3 19 | 3.33 | 4.01 | 3 17 | 3 96 |
| 7 | 0.84 | 1.17 | 1.05 | 2.02 | 2.14 | 2.19 | 3.12 | 1.88 | 2.42 |
| 8 | 1 09 | 0.86 | 0.87 | 1.37 | 1 68 | 1 36 | 1 72 | 1 40 | 1.85 |
| 9 | 1 06 | 0.82 | 0 79 | 1.01 | 1 17 | 1 18 | 1 11 | 0 95 | 1 31 |
| 10 | 0.40 | 0 66 | 0.71 | 0 38 | 0 80 | 1.08 | 1.10 | 0 85 | 1 15 |
| 11 | 0.23 | 0 71 | 0 50 | 0.35 | 0.79 | 0.58 | 0.80 | 0 64 | 0.84 |
| ≥12 | 70 58 | 57.27 | 58 14 | 52.22 | 44 52 | 43 52 | 37 02 | 43 70 | 37.28 |

We note here that a significant difference between our RMC results and the previous ones [17,18] is that we have covered a larger temperature range which allows us to follow the temperature evolution of all the properties that were previously studied close to the melting point. This enables us to draw some more inferences on the static structural properties of Se at those temperatures. In addition, we have used more recent and expectedly better data on the static structural properties of Se for the calculations.

Another important quantity that we analysed was the bond – angle correlation $b(\cos\theta)$. This is defined as the probability of two neighbours within $r_1$ from a central atom forming an angle $\theta$ with the central atom.

Figure 4 shows a plot of $b(\cos\theta)$ for Se over the temperature range we have investigated. From a perusal of the figure, one observes at the lowest temperature of 573 K, the existence of two peaks, one at $\cos\theta \approx -0.207$ and the other at $\cos\theta \approx 0.5$. The area under the first peak is however much larger than that at the second peak. With increasing temperature, the first peak at $\cos\theta \approx -0.207$ broadens out and eventually becomes structureless at high temperatures while the one at $\cos\theta \approx 0.5$ *i.e.* ($\theta \approx 60^0$) is still observable.

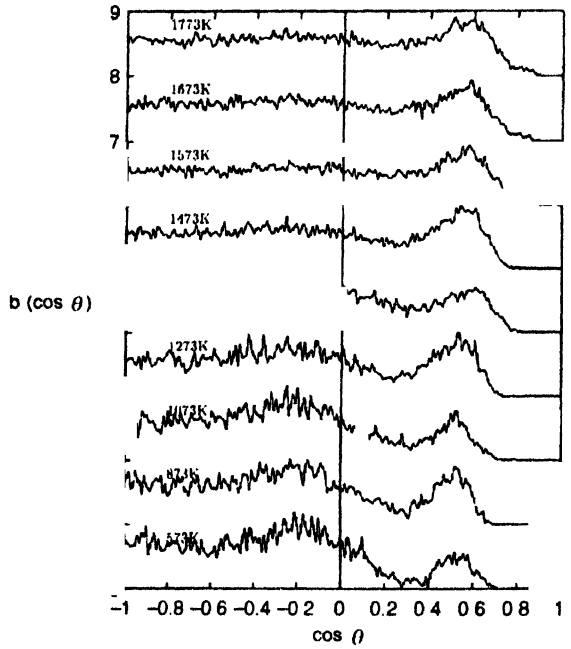


**Figure 4.** Bond angle distribution $b(\cos\theta)$ against $\cos\theta$ for Se.

The peak at $\cos\theta \approx 0.5$ *i.e* $\theta \approx 60^0$ is due to the existence of a small number of equilateral triangles with Se at each end of the triangle. One might feel that the occurrence of this $60^0$ peak is indicative of triplets of Se hard spheres. A relevant question here is whether the Se triplets with a bond angle of $60^0$ really exist naturally, particularly when one expects that most Se atoms would be two-fold coordinated. However, the fact remains that the experimental data allows a diversity of bond angles. One notes that the RMC simulation always generates the structure with the highest degree of disorder that a particular set of data allows. In addition, the presence of the Se triplets is essentially indicative [24] of a sharp peak in $g(r)$ as is observable in Figure 3.

The peak at $\approx 102^0$ indicates a relatively large bond angle and is the evidence of a relatively open structure for Se. In addition, this value of the bond angle is quite close to that for trigonal Se which is $103^0$ [8] and is the evidence of the fact that the short-range order in the liquid remains very similar to that in the solid. With regards to the increase and eventual blurring of the second peak in $b(\cos\theta)$ with increasing temperature, this appears to indicate that there is a gradual change in the structure of Se with increasing temperature.

The increase in the average bond angle is partly due to an increase in the bond angle for the two-fold coordinated atoms and partly to an increase of the fraction of 3-fold coordinated atoms for which the average bond angle is about $109^o$

In addition, our RMC results indicate that there is a decrease in the number of branched chains with an increase in temperature, their small concentration at high temperatures is probably related to the increase in the percentage of 1 and 3-fold coordinated atoms at high temperatures.

From the above findings, we infer that with increasing temperature, there is a decrease in density leading to the observed increase in the position of the first minimum in $g(r)$. Subsequently, slight increase of $N_c$ is affected by an expansion between and along the chains, subsequently many of the chains are broken. It follows that the observed metallic behaviour at higher temperatures would now be caused by the existence of an increased number of short-chains.

Regarding the three dimensional diagrams produced from the resultant configuration files, we present in Figure 5, 'ball' and 'stick' diagrams of them at some temperatures. Here, free Se atoms are shown as 'balls', while 'sticks' are bonds between Se atoms that are within a distance of 2.3 Å (the position of the first peak in $g(r)$) from each other. Some interesting features are visible from the figure.

At the initial temperature of 573K, there is a relatively large number of free atoms while one observes mostly simple bonds between Se atoms. We assume that this kind of configuration is indicative of a semiconducting state.

With increasing temperature, the number of unbonded atoms decreases significantly while most of them are bonded in some kind of chain like configuration and part of them appear to be made up of some kind of broken chain configurations. One is of the opinion that the broken chain configuration is partly responsible for the more metallic behaviour observed at such higher temperatures. This can be inferred from the predominance

of broken chains which appears in the configuration at a temperature of about 1373K.

increasing temperature, the system tends to exhibit both types of bonding while at higher temperatures, metallic bonds tend to

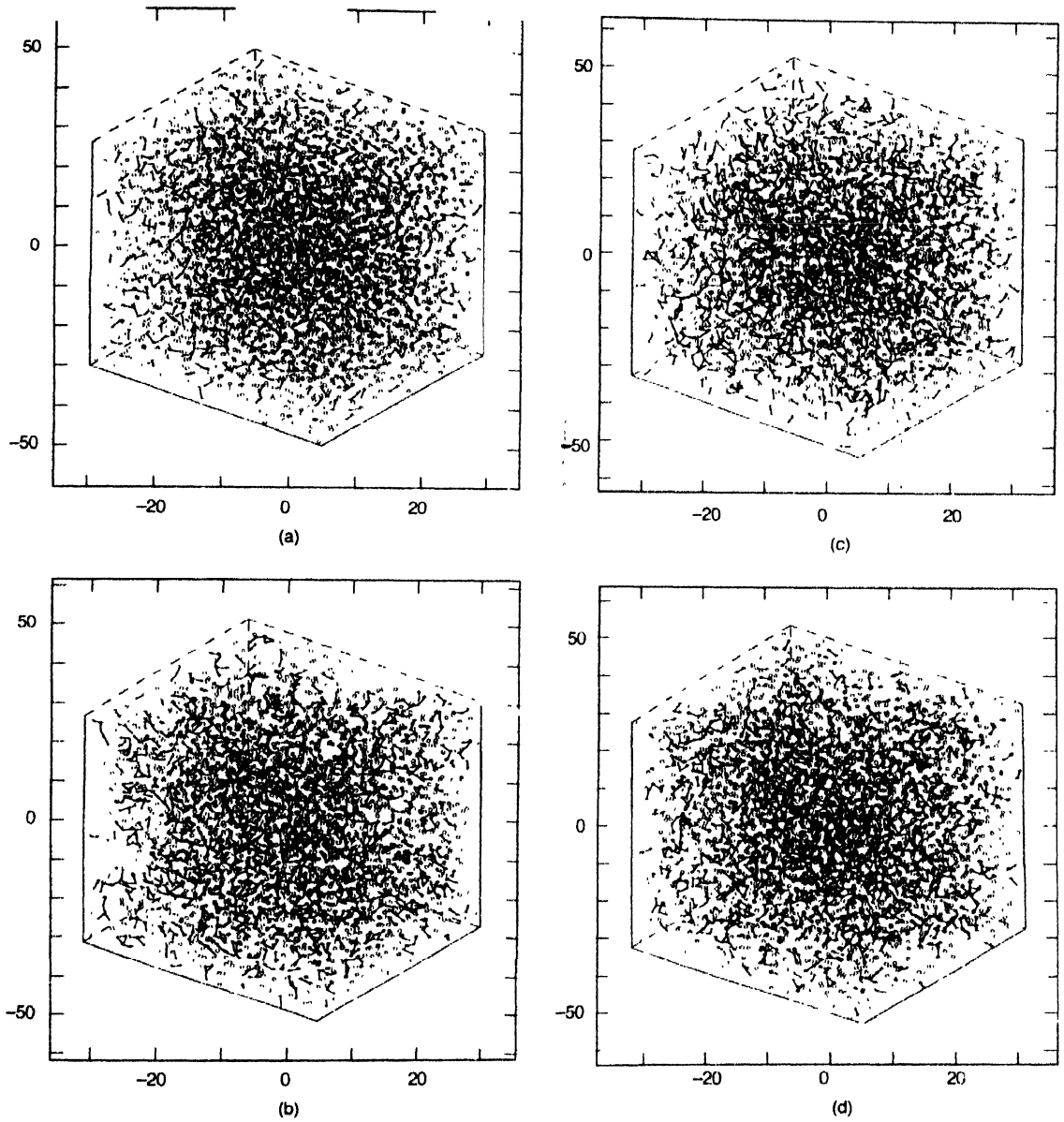


**Figure 5.** Configuration of Se obtained by RMC simulation for Se at (a) 573K , (b) 1273K, (c) 1573K and (d) 1773K

At 1373K, which is close to the transition temperature, one observes the occurrence of broken chains which are visible as multiple bonds between atoms in addition to the normal linear (chain) bonds. At temperatures at about 1573K and higher the number of broken chains by inference, the degree of metallic bonds tend to increase. The resultant effect of this is the occurrence of a more metallic behaviour.

Thus, one can infer from the above observations that the structure of Se at any instance consists of regions of metallic and semiconducting bonds. This is evident from the 3-dimensional pictures obtained from the resulting configuration files. At low temperatures, semiconducting regions are more dominant and are responsible for the SC properties. With predominate and thus Se becomes metallic. The whole process is quite gradual however, and this makes it difficult within the present framework to associate any particular physical characteristic with the critical point for Se.

## 4. Conclusions

A reverse Monte Carlo modelling of the structure of low density selenium spanning temperatures in the region of the semiconductor to metal transition, has been successfully performed. We have shown that the structure factors obtained from our simulation are in very good agreement with the experiment over the whole temperature range. From this, we expect that our three-dimensional picture of Se should give an accurate description of the real liquid.

Arising from an analysis of the atomic configuration, used to determine the structure, we have been able to show that low density Se does not expand uniformly but rather, as a result of a change in the coordination number around each atom. Furthermore, with an increase in temperature, there is a decrease in the fraction of 2-fold coordinated atoms and this is indicative of a shortening of the chain that makes up the structure of Se as temperature increases. However, our modelling indicates that the chain-like structure persists even in the metallic state. From a study of the bond angles, we are able to deduce that the transition from a semiconducting to a metallic state is accompanied by some degree of structural change.

We conclude by speculating that with increasing temperature, the density fluctuations close to the SC-M transition induce a shortening of the chains in Se. When the region consisting of the chains percolates over the fluid, the semiconducting fluid becomes metallic.

From our RMC calculations, we conclude that the transition from a semiconducting to a metallic behaviour in Se is a continuous process without any discontinuity.

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